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THE USE OF OXYGEN IN THE MANUFACTURE OF WATER GAS

BY

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ABSTRACT OF A THESIS

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ACKNOWLEDGEMENT

The writer wishes to express his sincere thanks to Professor S. W. Parr for the suggestion of this problem and for providing apparatus and space in the Experimental Fuel Plant where the work was carried on. The interest and cooperation he has given are greatly appreciated.

The assistance of Messrs. F. B. Hobart and T. Y. Cheng in taking readings was a valuable asset to the work and is appreciated.

Use of Oxygen in the Manufacture of Water Gas^{1,2}

By F. E. Vandaveer with S. W. Parr

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A large number of experiments using oxygen, steam, and coke for the manufacture of water gas have been made; also a number using oxygen and coke for making carbon monoxide. The conditions as to temperature ranges, pressures, thickness of fuel bed, and oxygen limitation for optimum production in both cases have been determined.

The reaction of oxygen and carbon to form carbon monoxide is the controlling reaction when carbon, oxygen, and steam are used for making water gas, because it produces heat for the decomposition of the steam and at the same time yields a combustible gas.

Calculations have been made showing that oxygen if obtainable at a cost of less than 25 cents per 1000 cubic feet could compete on an equal economic basis with air. If allowance is made for the advantages of the process a price of 50 cents per 1000 cubic feet might be paid.

From the data obtained a distribution of the factors involved have been made showing the amount of water gas obtained per ton of coke, the amount of oxygen used per ton of coke and per 1000 of gas, and the amount of steam used per ton of coke and per 1000 of gas. Similar calculations have been made for coal.

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THE use of oxygen or oxygenated air in the manufacture of water gas is of vital interest to all manufacturers of fuel gas because it presents the possibility of reduction in cost of manufacture. The present system of making water gas is very wasteful of the heat energy in the coal or coke used. This is due largely to the use of air during the blow period when the coke is heated to the temperature necessary to decompose steam during the make period.

¹ Received June 27, 1925. Presented before the Joint Meeting of the Divisions of Petroleum Chemistry and Gas and Fuel Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

² Abstract of a thesis submitted in partial fulfilment of the requirements for the degree of doctor of philosophy in chemistry in the Graduate School of the University of Illinois, 1925.

The gas during the blow period is high in inerts and cannot be used except in waste heat boilers. There is also an excessive loss of heat during the charging and cleaning periods. According to the Sixth Report of the Research Subcommittee of the Institute of Gas Engineers, the efficiency of water gas production with waste heat boilers is about 56 per cent. If oxygen were used in a complete gasification process so that the blow period could be eliminated we should expect an efficiency of 90 per cent. This would mean a saving of 34 tons of coal out of every 100 tons used. Although these figures give only approximate values, they are close enough to say that, whereas the present process would involve a loss of nearly one-half of the coal, the oxygen process would lose only one-tenth.

By the use of oxygen, water gas presumably could be made continuously. It would be similar to the continuous process of making producer gas, but the resulting gas would be much higher in calorific value, owing to elimination of the inerts ordinarily found in producer gas. Since the resultant gas from such a process would be a mixture of carbon monoxide and hydrogen, it will be discussed here as a water gas because of the relation of the reactions involved to the manufacture of that type of gas. It is proposed in this procedure (1) to use oxygen to produce heat in the generator by burning the oxygen and carbon to carbon monoxide, or to carbon dioxide with subsequent reduction to carbon monoxide; (2) to use steam to keep the temperature under control while at the same time utilizing the endothermic character of the reaction involved in the process of decomposing it into hydrogen and carbon monoxide. The cleaning and charging periods could be obviated because the process could be made continuous, the coal or coke being fed in continuously at the top, oxygen and steam being blown in at the bottom, while the ash would be melted or slagged off at the bottom or in some way removed continuously and the water gas taken off at the top of the generator.

A fundamental question at the outset will be—how cheap must oxygen become before it can be used economically by gas companies at the present prices of coal and gas? The following approximate figures may be used as a basis:

Efficiency of water gas plant is 56 per cent
 Efficiency of gasification plant using oxygen is 90 per cent
 Therefore, a saving of fuel per 100 tons gasified equals 34 tons
 Oxygen required per 100 tons fuel equals 1,250,000 cubic feet
 (55.74 tons)³

(An average of Tours, Jefferies, and Hodsman and Cobb's results)

Price of fuel equals \$6.50 per ton (West Virginia Gas Coal at the plant of the Champaign Gas Company)

Therefore, price payable for oxygen is $\frac{34 \times 650}{1250}$ cents per 1000 cubic feet—i. e., 17.7 cents

³ Willien, *Am. Gas Assoc. Monthly*, 5, 565 (1923).

From this relation it is seen that 17.7 cents per 1000 cubic feet of oxygen could be paid as a maximum cost for that material under the conditions indicated. It may also be pointed out that as the price of the coal used as generator fuel increases more may be paid for the oxygen. Thus, coal at \$10.00 a ton would permit the use of oxygen at 27.2 cents per 1000 cubic feet. Likewise, as the price of coal decreases the price paid for oxygen must decrease. Take, for example, the same West Virginia coal at the mine costs \$2.50 a ton. At that rate oxygen would have to be obtained at 6.79 cents per 1000 cubic feet. In considering the amount it is practicable to pay for oxygen, the capital investment must also be considered. It seems probable that an oxygen steam producer would greatly lower capital costs for gas companies; that is to say, the combined cost of the oxygen plant and the gasification plant should be less than the present carbonization-gasification unit. If this is the case more could be paid for the oxygen produced. It would seem to be a fair figure, if the advantages of the process were taken into account, to say that oxygen under 50 cents per 1000 cubic feet could be used profitably, but it should be under 25 cents per thousand to compete on an equal economic basis with air.

It was not the purpose of this article to deal with the various processes for obtaining cheap oxygen, but the direction from which we may expect it to come, the possibilities for obtaining it in the near future, and its application to the manufacture of water gas may be obtained from other articles.⁴

The purpose of this investigation was to make water gas using oxygen, steam, and coke, and to study the reactions involved, the temperature necessary for the reaction, the pressure, the rates of flow, the thermal relations, the composition of the gas produced, and the amounts of oxygen and steam used to make a measured amount of gas. It was undertaken on the assumption that cheap oxygen would some day be available and before that time comes we should know more about its use in the actual production of gas.

Apparatus

A small gas plant for making water gas was constructed as shown in Figure 1. It consisted of a generator, *A*, two condensers, *B*, two scrubbers, *C*, a Crowell centrifugal pump, *D*, a 10-light gas meter, *E*, for measuring the gas made, and two gas holders, *F*. The oxygen was supplied from 220-cubic

⁴ Hodsman and Cobb, *Gas J.*, **150**, 640 (1920); Jeffries, *New England Assoc. Gas Engineers*, 1921 Convention, p. 264; Müller, *Z. angew. Chem.*, **33**, I, 36 (1920); Norton, *Chem. Met. Eng.*, **23**, 511 (1920); Murray, *Trans. Faraday Soc.*, **18**, 205 (1922); Finlayson, "Industrial Oxygen," booklet printed by the Woodall-Duckham-Jones Vertical Retort Company; Willien, *Am. Gas Assoc. Monthly*, **5**, 565 (1923); Davis, *Bur. Mines. Repts of Investigations* **2502**, 33; Dyrssen, *Blast Furnace Steel Plant*, **12**, 162 (1924); Bauer, Report of Committee on Carbonization and Complete Gasification of Coal, *Am. Gas Assoc.*, 1924 Convention, p. 50; Porter, "Coal Carbonization," A. C. S. Monograph, pp. 64 and 365.

foot cylinders, and was measured by an Ox-weld pressure gage and a 10-light gas meter. The steam was generated from a weighed amount of water in boiler, G, by high pressure steam which passed through coils inside the boiler. The air was obtained from the university compressed air lines. The gas for igniting the coke at the beginning of the run was obtained from the city gas mains. The harp arrangement of pipes in front of the generator are, from left to right, primary air for gas burner, secondary air, steam to furnace, oxygen, secondary air, and city gas.

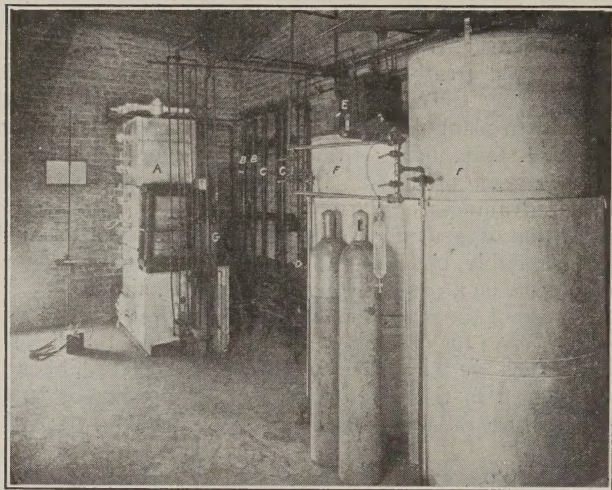


Figure 1—Experimental Gas Plant

The generator is shown in cross section in Figure 2. It was built of fire brick with fire clay for bonding. It was covered on the sides with No. 18 sheet metal welded to 2-inch angle irons on the corners. The top of the generator and the front of the projection at the bottom were covered with 0.25-inch plate iron welded to the sheet metal. Thus the generator was made gas-tight. The inside of the generator was 5.25 by 5.25 inches at the top, sloping to 9.5 by 5.25 inches at the place where the opening to the front of the generator began. This opening was 16.25 inches high by 5.25 inches wide by 31 inches long. Other dimensions may be obtained from the drawing.

Manipulation of Apparatus

In starting an experiment the generator was charged with a weighed amount of coke, a mark being made on the outside of the generator for the height to which every 5 to 10 pounds of coke came, in order to obtain roughly the amount of coke used during the run. The coke was then ignited by means of the gas burner. After the ignition of the coke at the bottom of the bed the gas was turned off and the air increased to blast

the coke. The heating of the generator and the coke to the right temperature for gas-making required about 6 hours.

In the experiments using oxygen and coke the oxygen was regulated as near as possible to 2.5 cubic feet per 5 cubic feet of gas made. During the run for every 5 cubic feet of gas made, readings were taken of amount of gas made, amount of oxygen used as recorded by the gage and by the meter, barometric pressure, temperature at I by the optical pyrometer, at II, III, and IV by color, the temperature of the exit gas by the thermocouple, and the pressure at the three gages.

At certain intervals during the run samples of gas were taken at outlet V, where the sample bottle is shown in Figure 1. One tank and eight sample bottles were generally used for collecting gas during a run. Some time during the run, generally during the first 10 or 15 cubic feet of gas made, samples of gas were taken simultaneously at the outlets on the side of the furnace and at outlet V.

The oxygen run lasted from 20 to 80 minutes, or until the temperature got so low that the gas being made was not very good. Oxygen was then shut off, the direction of the gas changed so that it was not sent through the meter, and the run was stopped. The height of the coke was measured and the oxygen run was completed.

For the oxygen-steam-coke run the same procedure in starting as in the oxygen run was used except that the oxygen was regulated at about 1.5 to 2 cubic feet per 5 cubic feet of gas made. The steam in the boiler was maintained as near 40 pounds pressure as possible and the valve on the steam line to the generator opened very slightly so that a small amount of steam was sent into the generator.

Reaction of Carbon and Oxygen to Form Carbon Monoxide

The controlling reaction in the use of oxygen for the manufacture of water gas is the carbon-oxygen reaction for forma-

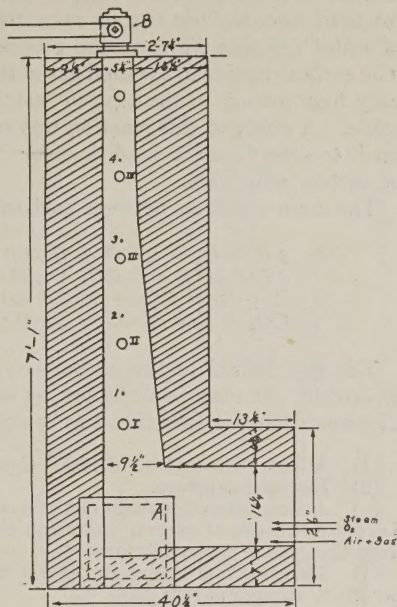
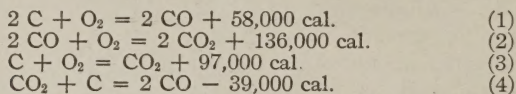


Figure 2—Cross Section of Gas Generator

tion of carbon monoxide, because (1) the heat for the process must be supplied from it, and (2) the formation of carbon dioxide is to be avoided. Unless carbon and oxygen can be made to react to form carbon monoxide under the conditions of water gas manufacture, the process cannot be a success. The carbon dioxide in the final gas of the first experiments was very high, owing to the oxygen reacting to form carbon dioxide. A study of this reaction was started and experiments made to determine the conditions for the optimum production of carbon monoxide.

The main reactions between carbon and oxygen are:



The gas desired in the carbon-oxygen reaction is carbon monoxide. It may be obtained by either Reactions 1 or 4. The conditions for Reaction 1 to be driven to the right are:

- (1) A high temperature of 1100° C. or more.
- (2) Reduced pressure.
- (3) A slow rate of passage of the oxygen through the carbon so that by reason of oxygen limitation there will be no alteration from the carbon monoxide formed.
- (4) This reaction begins to reverse only at a very high temperature, approximately 2500° C.

The conditions for Reaction 4 to be driven to the right are:

- (1) A high temperature of 1000° C. or more.
- (2) Reduced pressure.
- (3) A slow movement of carbon dioxide through the carbon at temperatures of 1000° to 1300° C. or more. Above 1300° C. the reaction goes to the right very rapidly.
- (4) This reaction reverses rapidly below 1000° C. and at 500° C. is almost completely reversed.

With these facts in mind a series of experiments using oxygen and coke were made. The results of two of them are given in Table I.

The data on Run A show:

- (1) A steady decrease in temperature as the run proceeds.
- (2) A value of 0.417 cubic foot of oxygen per cubic foot of gas made, which is below the theoretical amount, 0.500. This difference may be accounted for by the air drawn into the generator.
- (3) A steady increase in carbon dioxide as the run proceeds.
- (4) A fluctuation in oxygen.
- (5) A decrease in carbon monoxide to No. VIII, then an increase.
- (6) A narrow variation in hydrogen.
- (7) A marked fluctuation in nitrogen.

The data from Run B show that:

- (1) The temperature fell steadily throughout the run.
- (2) The oxygen 0.521 cubic foot per cubic foot of gas should have been sufficient to maintain the temperature.

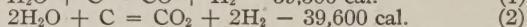
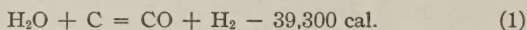
Table I—Manufacture of Carbon Monoxide
Operating data and gas analyses from two runs, using oxygen and coke, with a vacuum on the generator and a slow passage of oxygen through the coke

Constituents used	Run A		Run B		Operating Data		Run A		Run B	
	O ₂ and high-temperature coke	O ₂ and low-temperature coke	O ₂ and high-temperature coke	O ₂ and low-temperature coke	Temperature, ° C., at I	Temperature, ° C., at II	At III	At IV	Exit gas	Room temperature, ° C.
Length of run, minutes	35	35	55	0.521	At III	At IV	At IV	At IV	Exit gas	Barometric pressure, mm.
Cubic feet of oxygen used	40.5	40.5	55	0.521	At III	At IV	At IV	At IV	Exit gas	Barometric pressure, mm.
Oxygen per cubic foot of gas made	1.41	1.41	1.57	1.57	At III	At IV	At IV	At IV	Exit gas	Barometric pressure, mm.
Rate of oxygen, cubic feet per minute	1.41	1.41	1.57	1.57	At III	At IV	At IV	At IV	Exit gas	Barometric pressure, mm.
Pounds of coke	3.75	3.75	3.75	3.75	At III	At IV	At IV	At IV	Exit gas	Barometric pressure, mm.
Depth of fuel bed, feet	120	120	105.5	105.5	At III	At IV	At IV	At IV	Exit gas	Barometric pressure, mm.
Cubic feet of gas made	120	120	105.5	105.5	At III	At IV	At IV	At IV	Exit gas	Barometric pressure, mm.
<i>Gas Analyses</i>										
(Analyses in per cent)										
RUN A—SAMPLES TAKEN PROGRESSIVELY FROM I THROUGH X										
Gas:	I	II	III	V	VII	VII	Tank I	VIII	IX	X
CO ₂	3.2	7.7	5.5	8.3	9.0	10.9	12.7	12.2	13.2	14.7
O ₂	2.3	0.4	0.6	2.0	2.1	2.4	0.8	2.8	1.1	1.8
CO	80.1	86.3	85.7	77.1	77.9	69.8	62.7	66.2	77.0	70.0
H ₂	2.6	1.6	2.0	1.6	1.6	1.7	2.3	1.8	1.5	1.7
N ₂	11.8	4.0	6.2	11.0	9.4	15.2	21.5	17.0	7.2	11.8
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Combustible	82.7	87.9	87.7	78.7	79.5	71.5	65.0	68.0	78.5	71.7
B. t. u.	267.5	284.2	283.7	254.7	257.2	231.5	210.5	220.0	254.1	232.0
Temperature, ° C.	1000	1000	1000	1014 to 1007	1020 to 1014	980 to 977	977 to 895	885	876	876
RUN B—SAMPLES TAKEN CONTINUOUSLY FROM V THROUGH IX										
Gas:	V	VI	VII	Tank I	VII	VIII	IX	X		
CO ₂	9.6	16.3	19.0	22.5	19.7	19.7	26.9	26.9		
O ₂	1.9	1.4	2.4	1.7	3.8	3.8	2.1	2.1		
CO	69.8	71.3	61.8	63.5	56.9	56.9	57.4	57.4		
H ₂	3.0	2.1	1.8	1.9	2.0	2.0	2.0	2.0		
N ₂	15.7	8.9	15.0	8.4	17.2	17.2	11.6	11.6		
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0		
Combustible	72.8	73.4	63.6	67.4	59.3	59.3	59.4	59.4		
B. t. u.	235.3	237.8	205.9	218.2	191.8	191.8	192.5	192.5		
Temperature, ° C.	1020 to 980	992 to 981	977 to 923	904 to 867	876 to 861	876 to 861	857 to 876	857 to 876		

- (3) The carbon dioxide gradually increased, No. VIII being an exception.
- (4) The oxygen varies within narrow limits.
- (5) The carbon monoxide varies but on the whole decreases as the carbon dioxide increases.
- (6) The hydrogen remains fairly constant.
- (7) The nitrogen varies considerably.

These results are typical of all oxygen-coke runs and indicate that in actual practice there is great difficulty in keeping the temperature high enough to produce carbon monoxide. As the temperature falls the carbon dioxide increases and the carbon monoxide decreases. If the oxygen was increased to keep up the temperature, the movement of the oxygen through the carbon was too fast and a high carbon dioxide percentage was obtained because condition (3) was violated. Perhaps a generator with a large diameter which would minimize channeling of the gases would reverse these results. However, it is very difficult to meet the first two conditions and at the same time meet the third one. If any one of the four conditions are violated the carbon dioxide content will be high.

Main Reactions between Carbon and Steam to Form Water Gas

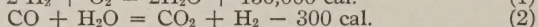
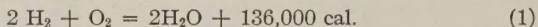


The gases desired in the carbon-steam reaction are carbon monoxide and hydrogen. The conditions for Reactions 1 and 2 to be driven to the right are:

- (1) A temperature above 900° C. Heat must be supplied to the reactions because they are endothermic.
- (2) Reduced pressure.
- (3) Both Reactions 1 and 2 are reversible, but neither 1 nor 2 is complete nor can it take place by itself, but in the presence of water and carbon the carbon monoxide and carbon dioxide interact with the excess carbon.

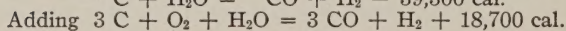
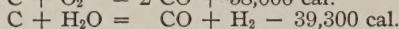
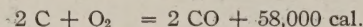
Primary Reactions between Carbon, Oxygen, and Steam

The main reactions between these three constituents involve the above six reactions and two others of a secondary nature, namely:

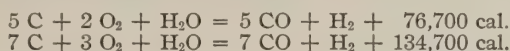


These two reactions are secondary reactions between gases and would not play an important part if the conditions outlined above for maximum production of carbon monoxide and hydrogen were followed.

The reactions of carbon, oxygen, and steam may be obtained by combining Reaction 1 under the carbon-oxygen reactions and Reaction 1 under the carbon-steam reactions.



In order to increase the heat liberated we must increase the amount of oxygen used, therefore, we may double or triple the oxygen-carbon reaction according to the following equations:



Theoretically, the last reaction should produce sufficient heat to keep the carbon-oxygen-steam reaction continuous. The conditions for the reaction to go to the right are:

- (1) A high temperature of the entire coke bed of 1000° C. or higher.
- (2) A reduced pressure.
- (3) A slow rate of passage of the oxygen and steam through the coke bed.
- (4) A carefully regulated ratio of oxygen to steam in order to maintain the heat balance.
- (5) An intimate mixture of oxygen and steam so that the heat absorbed by the steam-carbon reaction would be more than counterbalanced at that point by the liberation of heat in the oxygen reaction.

With these facts in mind a number of experiments using oxygen, steam, and coke were made. The results of two of them are given in Table II.

The following facts may be pointed out concerning Run A:

- (1) A rapid decrease in temperature as the run proceeded. The temperature at the beginning was low.
- (2) An increase in carbon dioxide as the run proceeded.
- (3) A fairly constant oxygen content.
- (4) A variation in carbon monoxide due to variations in hydrogen and nitrogen.
- (5) A variation in hydrogen due to a change in amount of steam used.
- (6) A variation in nitrogen.

The data from Run B show that:

- (1) The temperature fell rapidly as the run proceeded. The starting temperature was very low.
- (2) A marked increase in carbon dioxide as the run proceeded.
- (3) A fairly constant oxygen content as the run proceeded.
- (4) In general, a decrease in carbon monoxide as the run proceeded.
- (5) A reasonably constant hydrogen content as the run proceeded.
- (6) A constant amount of nitrogen within narrow limits. In no case in this run does the nitrogen content figure up with the oxygen content as air. Therefore, some oxygen must have carried through the fuel bed.

These results are typical of the oxygen-steam-coke runs. They indicate that in actual practice a careful regulation of the oxygen-steam ratio must be observed and that a slow passage of the gases through the coke is necessary. In both of these runs the carbon dioxide content became very high at the latter part of the run because the temperature fell. It is seen from the equations already given that three times as much oxygen as steam must be used to keep up the heat

Operating data and gas analyses from two runs, with a vacuum on the generator and a slow passage of oxygen and steam through the coke

[illegible]

of the reaction. Therefore, this oxygen must be nearly 100 per cent converted to carbon monoxide; and to do this a very strict regulation must be maintained and all the conditions of the oxygen-carbon reaction to form carbon monoxide must be met. A few difficulties not pointed out by the equations but which are characteristic of the oxygen-carbon reactions are:

- (1) A very shallow zone of reaction.
- (2) An almost instantaneous reaction.
- (3) If the passage of the oxygen through the coke is too fast the combustion goes to carbon dioxide and then when it strikes the zone of coke above the hot zone of reaction it is not reduced to carbon monoxide and therefore remains as carbon dioxide in the final gas.

Ash Disposal

The disposal of the ash was not studied in detail, but some observations were made. The ash from Illinois coal melted very easily into a dense, hard clinker. This was also true of the ash from Alabama coke. In fact, the temperature was so high at times that globules of melted ash were seen falling down through the coke. Since the ash from Alabama coal melts around 1650° C., which is nearly as high as any coal ash in this country, it seems very probable that all coal ash would melt in the oxygen process.

Calculations

The results of Run A in Table II using the gas analysis of Tank II have been figured on the basis of a ton of coke and are given in Table III.

With raw coal as the initial material the reactions discussed would not be essentially different; the results therefore referred to coal would be a matter of calculations, which are not here included.

Table III—Results Obtained on Gasification of Coke Using Oxygen and Steam with a Vacuum on the Generator

Cubic feet of gas per ton of coke	66,000
Pounds steam required per ton of coke	920
Pound steam required per M of gas	13.95
Cubic feet of oxygen required per ton of coke	20,562.0
Cubic feet of oxygen required per M of gas	311.6
Composition of gas, per cent:	
Carbon dioxide	10.4
Illuminants	0.0
Oxygen	0.6
Carbon monoxide	57.6
Hydrogen	20.7
Methane	0.0
Nitrogen	10.7
Total	100.0
B. t. u.	253.5

VITA

The writer was born at the village of Athensville, Illinois, on November 29, 1899. At the age of five, his family moved to White Hall, Illinois. The next year he entered the White Hall Public School and continued there till the sixth grade was reached. The sixth grade work was taken at the country school of Mt. Airy, Illinois. The seventh and eighth grade work was taken at the White Hall Public School.

In the Fall of 1913 he entered the White Hall High School, from which school he was graduated in 1917 as valedictorian of the class.

From September, 1917 to June, 1919, he attended Illinois Wesleyan University at Bloomington, Illinois. He was enlisted as a private in the S. A. T. C. while there in the Fall of 1918.

In September, 1919, he entered the University of Illinois and has continued there to date. In February, 1922, he received the B. S. degree and in June, 1923, the M. S. degree.

He was Research Graduate Assistant in Gas Engineering at the University of Illinois from February, 1922 to June, 1924. The present school year he has a Graduate School Fellowship in Chemistry. During the summers of 1922 and 1923 he was cadet engineer with the Peoples Gas Light and Coke Company of Chicago.

Papers include: "An Improved Apparatus for the Analysis of Fuel Gas," Industrial Section of the Intersectional meeting of the American Chemical Society at the University of Illinois, May, 1923.

"An Apparatus for the Complete Analysis of Fuel Gas" with S. W. Parr, Gas and Fuel Section of the American Chemical Society, meeting at Milwaukee, 1923.

Publications include:

"Gas Plant Work." Illinois Chemist, November, 1922.

"The Analysis of Fuel Gas" with S. W. Parr, Circular No. XII, Eng. Exp. Station, University of Illinois.



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